

FORNICATION  
OF THE  
DOCUMENTS  
ARE  
ILLEGAL

**TITLE:** THE UTILIZATION OF SOLAR THERMAL SOURCES FOR THERMOCHEMICAL HYDROGEN PRODUCTION \*

**AUTHOR(S):** Melvin G. Bowman

**MASTER**

**SUBMITTED TO:** Presented at the AS/ISES 1980 Annual Meeting  
"The Solar Jubilee - 25 years of the sun at work,"  
Phoenix, Arizona, June 2-6, 1980. To be published  
in the "Proceedings."

\*Work supported by the U. S. DOE, Division of Basic Energy Sciences.



By acceptance of this article, the publisher recognizes that the U.S. Government retains a nonexclusive, royalty free license to publish or reproduce the published form of this contribution, or to allow others to do so, for U.S. Government purposes.

The Los Alamos Scientific Laboratory requests that the publisher identify this article as work performed under the auspices of the U.S. Department of Energy.

University of California



**LOS ALAMOS SCIENTIFIC LABORATORY**

Post Office Box 1663 Los Alamos, New Mexico 87545

An Affirmative Action/Equal Opportunity Employer

## THE UTILIZATION OF SOLAR THERMAL SOURCES FOR THERMOCHEMICAL HYDROGEN PRODUCTION

Melvin G. Bowman  
Los Alamos Scientific Laboratory  
Los Alamos, NM 87545

### ABSTRACT

The utilization of high temperature solar heat for the production of electricity and/or fuels is a popular concept. However, since solar concentrator systems are expensive and solar radiation intermittent, practical utilization requires processes that exhibit high conversion efficiencies and also incorporate energy storage. The production of hydrogen fulfills the requirement for energy storage and can fulfill the requirement for efficient heat utilization if thermochemical cycles are developed where the temperature and heat requirements of the process match the heat delivery characteristics of the solar receiver system. Cycles based on solid sulfate decomposition reactions may lead to efficient utilization of solar heat at practical temperatures. Higher temperature cycles involving oxide decomposition may also become feasible.

### 1. INTRODUCTION

The utilization of solar energy for the production of fuels and chemicals is a popular concept that appears to be attracting an increasing constituency. Certainly the concept merits serious consideration despite the fact that solar concentrator systems are expensive and solar heat intermittent. It must be recognized, however, that the practical utilization of high temperature solar heat will require systems and processes that exhibit high conversion efficiencies and that also incorporate energy storage. Since hydrogen fulfills the requirement for energy storage, is itself an attractive transportable fuel and is the "prime intermediate" in the production of many fuels and chemicals, significant effort should be directed to the development of hydrogen production processes that interface with high temperature solar systems to give efficient heat utilization.

The advantages of hydrogen have been generally recognized and more efficient methods

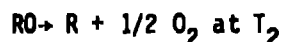
for utilizing primary heat sources to decompose water are the objectives of cooperative research and development programs under the International Energy Agency. The electrolysis of water is well known and two of the I.E.A. programs are directed toward the development of more efficient and less costly electrolysis processes. One program is concerned with improving the electrolysis of acidic and basic solutions at relatively low temperatures. The second is concerned with the high temperature electrolysis of steam where stabilized zirconia serves as a solid electrolyte (1). However, efficiencies for electrolytic hydrogen production will be limited by efficiencies for producing electricity and it is clear that adaptation of existing power production methods to solar heat sources will give low efficiencies. Therefore, the development of more efficient, high technology processes for efficient power production will be necessary before electrolysis can be coupled to solar heat sources in a realistic way.

One of the important I.E.A. programs for hydrogen production is concerned with coupling thermochemical and hybrid thermochemical water splitting cycles to primary heat sources. This I.E.A. activity reflects the wide recognition that thermochemical cycles offer the promise of high efficiency for the utilization of high temperature process heat to decompose water. It is also important to note that the development of thermochemical cycles specifically for solar heat sources has been identified recently as one of the areas for cooperation under the I.E.A. agreement on hydrogen production. Thus, it is realized that the characteristics of the heat delivery will determine the criteria required if the process is to couple efficiently with the solar concentrator. The purpose of this paper is to define the "ideal criteria," to describe valid cycles developed over the years in terms of the criteria and to examine cycles being considered for adaptation to high temperature solar heat.

## 2. CRITERIA FOR IDEAL CYCLES

One method for defining thermodynamic criteria for efficient cycles, in terms of "ideal" enthalpies and entropies has been presented several times. It is presented again here as background for the selection of thermochemical cycles for solar heat sources.

Consider a two-step (single temperature cycle) process in which a reactant (R) reduces water at a low temperature ( $T_1$ ) to evolve hydrogen and form the compound RO (R may also be an oxide), followed by thermal decomposition of RO at high temperature ( $T_2$ ) with the evolution of oxygen. The reactions can be written as:



If an ideal cycle is considered to be one in which  $\Delta G^0 = 0$  for all reactions, and if one utilizes the approximation

$$\Delta G_T^0 = \Delta H_{298}^0 - T \Delta S_{298}^0$$

"ideal" values for entropies and heats of formation of the compound RO are approximately defined by the expressions:

$$\text{"ideal"} \quad \Delta S_F^0 = \frac{\Delta G_F^0 (H_2O)}{(T_2 - T_1)}$$

$$\text{"ideal"} \quad \Delta H_F^0 = \Delta S^0 \times T_2$$

where  $\Delta G_F^0 (H_2O)$  is the free energy of formation of water at  $T_1$  (the low temperature). To illustrate, if we assume  $T_1 = 400$  K (where  $\Delta G_F^0 (H_2O) = 224$  kJ), and assume different temperatures for  $T_2$ , the corresponding parameters computed for RO are listed in Table 1.

Table 1.

$T_2$	$-\Delta S_F^0$ (RO)	$-\Delta H_F^0$ (RO)
1200	280 JK <sup>-1</sup>	336 kJ
1500	204	306
2000	140	280
2500	107	268

Since entropies of formation of oxides (per oxygen atom) are characteristically near -100 JK<sup>-1</sup> it is clear that very high temperatures will be required for two-step oxide cycles. This observation is the basis for published statements that two-step cycles are not feasible. Actually, two-step cycles are possible, in principle, even for relatively low maximum temperatures if one can identify usable reactions with the necessary large entropy changes. It should be emphasized that the entropy changes listed are minimum absolute values. Low temperature

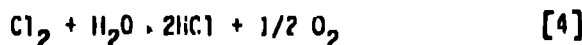
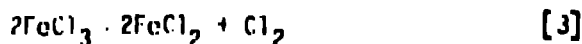
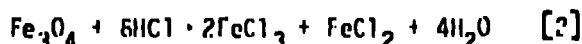
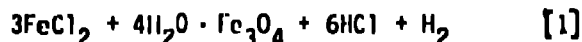
reactions cannot be expected to occur at a reasonable rate unless the free energy change is significantly negative. Thus, low temperature reactions must be more exothermic than indicated and, consequently, the high temperature reactions will be more endothermic.

## 3. OVERVIEW OF CYCLE DEVELOPMENT

During the past few years, thermochemical hydrogen production has been a popular topic and literally hundreds of cycles have been proposed and published. Unfortunately many of the proposed cycles are not thermochemically valid and a large fraction of those based on sound thermochemistry have been found to exhibit slow reactions. Thus, it is not surprising that most of the cycles given serious developmental efforts were not originally identified by application of the criteria described above. However, the criteria can be used to determine whether cycles that have been demonstrated experimentally are suitable for adaptation to solar heat sources.

### 3.1 Halide Hydrolysis Cycles

For several years most of the process development effort on thermochemical cycles was devoted to the iron chloride cycle. Several different laboratories appeared to claim origin of the cycle. The Institute of Gas Technology version of the cycle may be described by the following equations (2).



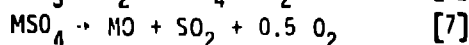
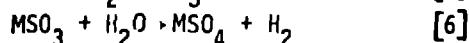
With respect to the criteria described above, the cycle is not attractive for any heat source. The  $\Delta S^0$  for reaction 1 is about 315 JK<sup>-1</sup>. This is larger than the ideal value listed for a 1200 K cycle (the temperature quoted for reaction 1), but the yield for the reaction is low which implies that  $\Delta H$  for the reaction is much larger than the ideal value. In addition, reactions 3 and 4 are also endothermic with positive entropy changes. Reaction 3 must be conducted as a cyclic decomposition with low yield in each cycle. The hydrogen from reaction 1 is mixed with hydrogen chloride and the necessary separation step requires additional expenditure of energy. Finally, a gaseous separation of oxygen and chlorine is necessary after reaction 4.

Alternate versions of the iron chloride cycle were promoted at different laboratories and other cycles involving halide hydrolysis reactions were experimentally demonstrated. Some of the cycles avoided part of the

difficulties listed for the iron chloride cycle, but none approximate the criteria needed for high efficiency and none appear to be attractive for use with a solar heat source. Of course, new halide cycles that incorporate practical solutions to the above problems might still be developed.

### 3.2 Oxide-Sulfate Cycles

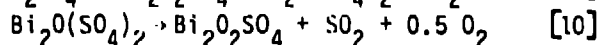
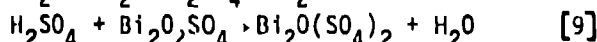
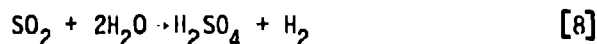
These cycles were developed from attempts at LASL to use the criteria described above to identify cycles with a minimum number of reaction steps and maximum temperatures below 1300 K. Since  $\Delta S^\circ$  values for decomposition reactions increase with the number of gaseous molecules evolved, studies were directed toward cycles involving the decomposition of sulfates (3). The concept can be illustrated by the following equations:



Equations 5 and 6 represent low temperature reactions. The typical  $\Delta S^\circ$  of the overall sulfate decomposition, reaction 7, is  $-275$  to  $-290 \text{ JK}^{-1}$ . This suggests the possibility of a two step cycle with an "ideal" temperature difference of  $800^\circ$  between low and high temperature reactions (see Table 1). Of course, larger temperature differences would be necessary. It should be noted that reactions 5 and 6 do not represent equilibrium. However, most sulfites form and decompose without evidence of the equilibrium reactions. Therefore, we were encouraged to attempt to promote reaction 6 in many different sulfate systems representing a wide range of stability. Our results have never included significant hydrogen yields. In most cases, the equilibrium reactions (sulfur or sulfide formation) were also not observed.

As a variation of sulfate cycles we also studied cycles based on the formation and decomposition of sulfuric acid. Several reactions to form sulfuric acid solutions were promoted successfully. Such cycles are currently receiving the major fraction of the worldwide development effort committed to thermochemical hydrogen processes. It should be noted that the overall decomposition of sulfuric acid includes a solution concentration step, an evaporation step to form  $H_2SO_4(g)$ , a decomposition step to form  $H_2O(g)$  plus  $SO_3(g)$  and the decomposition of  $SO_3$  to form  $SO_2$  plus  $0.5 O_2$ . Since homogeneous decomposition reactions occur over significant ranges of temperature, the overall process accepts heat over a wide temperature range with the maximum temperature dependent on the pressure of the system. It should also be noted that these processes

yield the acid in aqueous solution and significant energy is required to concentrate the acid prior to the decomposition step. Thus, sulfuric acid cycles are compatible with the heat delivery characteristics of gas-cooled reactors. However, if sulfuric acid cycles are coupled to solar heat sources, the unique features of such heat sources (higher temperatures and the availability of isothermal heat) will be compromised and potential higher efficiencies may be sacrificed. One possible method for utilizing the unique heat delivery characteristics of solar systems and also minimizing low temperature heat requirements for sulfuric acid systems involves reacting the sulfuric acid solution with a metal oxide to form an insoluble sulfate. For highest efficiencies, the metal sulfate should be insoluble, should not form a hydrate and should not require excessive heat for its decomposition (i.e., should decompose near the  $SO_3$  decomposition temperature). The LASL bismuth oxysulfate cycle is an example of the application of the concept to the hybrid sulfuric acid cycle. It may be described by the reactions:



Reaction 8 represents the electrochemical reaction to form dilute sulfuric acid and hydrogen. Reaction 10 is an endothermic reaction with  $\Delta G^\circ$  near zero at 1050 K and a heat requirement of about 270 kJ for each mole of  $SO_2$  produced. It should be apparent that the heat requirement for reaction 10 is much lower than that required for the high temperature step of a two step cycle. Of course, the additional energy needed is part of the large energy requirement for the overall process of forming sulfuric acid and evolving hydrogen whether it is via an electrochemical step or whether it includes a sub-cycle to form and decompose a hydrogen halide. Unfortunately, the energy involved in forming sulfuric acid is higher than desired and one important area for further research is the development of methods to minimize this energy requirement.

It seems probable that bismuth may not prove to be the best candidate for sulfate cycles. In addition to the fact that bismuth is quite expensive, there is the possibility that a more stable sulfate will be better suited to reducing the energy required for some overall process to form dilute sulfuric acid and evolve hydrogen. The elimination of sulfuric acid as an intermediate might be sufficiently advantageous to justify use of more stable sulfates that require isothermal heat at temperatures near the practical maximum for solar concentrator systems. Thus, continuing research on sulfate systems is a part of the LASL program.

#### 4. HIGH TEMPERATURE CYCLES

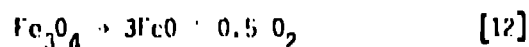
The high stagnation temperatures quoted for solar furnaces appear to be the basis for some of the very high temperature water splitting cycles that have been proposed. For example the decomposition of  $H_2O(g)$  has been proposed many times even though it is clear that the low entropy change associated with this homogeneous decomposition reaction implies a low reaction yield even for the maximum credible temperature listed for a practical solar heat source. This was recognized by Fletcher and Moen (4) who proposed operation at low pressures to enhance reaction yields. They also recognized the necessity of separating the hydrogen and oxygen at temperature in order to avoid the extremely rapid back reaction as the gases are cooled and proposed a separation based on the differences in effusion rates through a ceramic membrane or gauze. However, for temperature limitations imposed by materials properties as well as radiation losses, decomposition yields remain low (even for the proposed low pressures) and realistic assessments indicate efficiencies for heat utilization are too low for practicality.

The direct thermal decomposition of carbon dioxide seems to offer advantages over water decomposition for a high temperature process since, at temperatures above 1100 K, decomposition yields are significantly higher. The dry gases could be quenched to lower temperatures by means of a nozzle expansion without excessive back reaction. However, in order for this process to be of value, a practical low temperature method for separating carbon monoxide from oxygen and for separating carbon dioxide from hydrogen would be required. Further, it would be necessary to dry the carbon dioxide before each high temperature step since traces of water greatly accelerate the oxygen-carbon monoxide reaction at high temperature.

In summary, it seems probable that the problems associated with the direct decomposition cycles are, and will continue to be, more difficult than problems associated with including additional reactions in cycles that permit lower temperature operation and still yield high efficiencies if the ideal cycle criteria can be approximated.

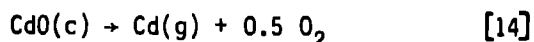
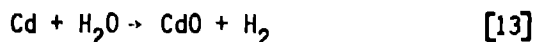
##### 4.1 Oxide Decomposition Cycles

A two-step iron oxide water splitting cycle has been proposed several times for use with high temperature solar heat. The cycle may be described by the following reactions:



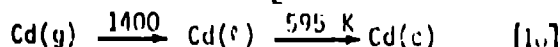
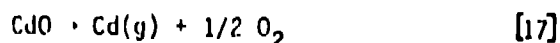
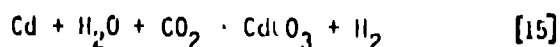
Reaction 11 is a known reaction. Reaction 12 (if written as a solid decomposition) exhibits one of the largest entropy changes known for this type of reaction. However, as Tofiqhi and colleagues found (5),  $Fe_3O_4$  melts before it decomposes and oxygen evolution occurs over a relatively narrow liquid homogeneity range at 2150 K. This is unfortunate, perhaps, since suitable candidates for this type of cycle have not been identified. Indeed, at the present time, attractive multi-step cycles that include a solid-solid oxide decomposition step have not been developed.

A second type of two-step, oxide cycle includes a solid decomposition reaction to form two gaseous products rather than a condensed phase and gaseous oxygen. The extra gaseous product increases the decomposition entropy and this implies a lower temperature process. The concept can be illustrated by the following equations for a cadmium oxide cycle:



This cycle has been proposed several times (and even patented) despite the fact that, for published thermochemical data, reaction 13 should not be expected and, in fact, does not occur. However, in 1976 Pangborn (6) of IGT described an electrochemical method for promoting the reaction. The proposed cycle was not developed into an actual process since projected gas cooled reactors (the "target" heat sources at that time) were not suitable for the high temperature isothermal step, even for the lower  $CdO$  decomposition temperatures sometimes reported. The cycle is now receiving renewed attention at IGT for use with a solar heat source.

At IASL, a "pure" thermochemical cycle is under study that also incorporates the decomposition of cadmium oxide (7). It may be described by the following reactions:



Reaction 15 to form the carbonate does take place, but the yield is limited by the formation of a protective layer of carbonate on the cadmium metal. However, encouraging results have been achieved in reactions where  $NH_4Cl$  is used as a catalyst for the reaction. The cadmium oxide based cycles offer the potential for high efficiency if:

- (1) Solar heat can be utilized effectively for the oxide decomposition step at temperatures near 1800 K.

- (2) The back reaction between cadmium vapor and oxygen is sufficiently slow.
- (3) The low temperature reaction can be conducted at a practical rate and the resultant solid does not adsorb or occlude too much water.

Certainly, one should add that the decomposition step requires a temperature that will probably not be available soon from practical solar process heat systems and that problems of reactor materials for such high temperatures may be very difficult. Nevertheless, the cadmium cycles appear to offer sufficient promise to justify additional development.

## 5. REFERENCES

- (1) Doenitz, W., Schmidberger, R., Steinheil, E., and Streicher, R., "Hydrogen Production by High Temperature Electrolysis of Water Vapor," Proceedings of the 2nd World Hydrogen Energy Conference (Pg 403), Zurich, Switzerland, Aug. 21-24, 1978.
- (2) Gahmer, J., Mazumder, M., and Pangborn, J., "Experimental Demonstration of an Iron Chloride Thermochemical Cycle for Hydrogen Production," Proceedings of the 11th IECEC, State Line, Nevada, Sept. 12-17, 1976.
- (3) Bowman, M., "Fundamental Aspects of Systems for the Thermochemical Production of Hydrogen from Water," Proceedings of the ANS First Topical Meeting on Nuclear Process Heat Applications, Oct. 1-3, 1974, Los Alamos, NM. (Los Alamos Scientific Laboratory Report No. LA-5795-C).
- (4) Fletcher, E. A., and Moen, R. L., "Hydrogen and Oxygen from Water," Science, 197, 1050 (1977).
- (5) Toffghi, A., Siblaude, F., Duccarroir, M., and Benezech, G., Rev. Int. Haes Temp. Refract., Vol. 15, 7-13 (1971).
- (6) Pangborn, J. B., "Laboratory Investigations on Thermochemical Hydrogen Production," Proceedings of the 1st World Hydrogen Energy Conference, Miami, Florida (1976).
- (7) Mason, C.F.V., and Bowman, M. G., "The Cadmium-Cadmium Carbonate Cycle for the Thermochemical Production of Hydrogen." To be published in the Proceedings of the 3rd World Hydrogen Energy Conference, Tokyo, Japan, June 23-26, 1980.